

Application No. 10/559,769
Attorney Docket No. 4385-053487

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/559,769 Confirmation No: 8049
Applicant : Frank Schröder et al.
Filed : June 28, 2006
Title : Method and Device for Producing Melamine in a Single-
Phase Tubular Reactor
Art Unit : 1624
Examiner : Venkataraman Balasubramanian
Customer No. : 28289

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. §1.131

I, Dr. Frank Schröder, hereby declare as follows:

1. I am one of the named inventors of the invention described and claimed in the above-identified application entitled "Method and Device for Producing Melamine in a Single-Phase Tubular Reactor". The present application is the U.S. National Phase application of PCT Application No. PCT/EP04/005882, filed June 1, 2004, which claims priority to German Application No. 10326827.8, filed June 12, 2003.

2. I studied chemical engineering at the Technical University of Leuna-Merseburg from 1985 to 1990. I received my Ph.D. in 1995 in the field of gas catalysis from the Martin Luther Universität Halle-Wittenberg.

3. Between 1995 and 2000 I worked as a scientific researcher at the Martin Luther Universität Halle-Wittenberg. I have worked for the Assignee of the present application,

AMI Agrolinz Melamine International GmbH since October 1, 2000. I am now the head of the high-pressure lab of the Assignee. I have been involved in several projects which have resulted in issued patents. I am currently the project leader for new melamine synthesis and the foundations of high pressure melamine production.

4. Before the filing date of the priority German Application to the present application, experiments were conducted under my supervision involving the subject matter of the present invention in a miniature autoclave. Further experiments were conducted under my supervision to explore the relationships between pressure, temperature and density conditions on the production of melamine. The melamine synthesis concept of the present invention was formulated and I submitted my concept to my employer, the Assignee of the present application, via a "Notice of Invention" Report before June 5, 2003. With the "Notice of Invention" Report, I also submitted a detailed discussion of the subject matter of the Report to my employer. My employer confirmed receipt of my "Notice of Invention" Report and requested that I assign the rights to the invention contained therein to them. A copy of my original "Notice of Invention" Report, including my detailed discussion of the subject matter of the Report, and my employer's assignment request are attached hereto as Exhibit A. Additionally, certified English-language translations of these documents are attached hereto as Exhibit B. The dates on the documents have been redacted.

5. From prior to June 5, 2003 until the filing date of the priority German Application to the present application, I proceeded diligently to seek patent protection on my invention contained in the "Notice of Invention" Report. Specifically, I worked with my co-inventors and German patent attorneys to prepare and file a German patent application directed to the subject matter of my "Notice of Invention" Report. Subsequently, corresponding PCT Application No. PCT/EP04/005882 was filed on June 1, 2004 directed to the subject matter of my "Notice of Invention" Report, and the present application is the corresponding U.S. National Phase application of PCT Application No. PCT/EP04/005882.

6. The aforementioned activity and conduct demonstrates the required evidence of conception and diligence to a subsequent constructive reduction to practice with respect to the invention of the present application.

7. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Frank Schröder
Dr. Frank Schröder

06. 12. 2007
Date

Erfindungsmeldung

A23D

Melamin-
Rohrreaktor

vom (Haupt)-Erfinder auszufüllen:

Hiermit gebe ich die im folgenden beschriebene Erfindung bekannt, für die ich um Beantragung des Patentschutzes im Namen des Unternehmens Agrolinz Melamin GmbH ersuche.

VERTRAULICH**10. Erfindungsgegenstand:**Titel des
Entwurfes der
Patent-
anmeldung:

Melamin in einer kontinuierlichen Phase im Rohrreaktor
aus Harnstoff

11. Technisches Problem, das die Erfindung behandelt?

Melamin erzeugen in einer kontinuierlichen Phase im Rohrreaktor
- geringere Reaktionswärme - geringerer Aufwand im HD-Teil - geringes
Gefahrspotential durch kurze Verweilzeit im HD-Teil

12. Beschreibung der Erfindung:

Harnstoff → → Melamin
CO₂, NH₃, NH₂COONH₄
Harnstoff (bis 15%)
600-800 bar ca 400°C

13. Was ist die Neuheit und der Vorteil der Erfindung?

Neuheit:

Einphasige Prozessführung unter schonem Druck im Rohrreaktor

Vorteil(e):

geringere Reaktionswärme, geringerer Aufwand im HD-Teil
geringeres Gefahrpotential durch kurze Verweilzeit im HD-Teil

14. Welcher Stand der Technik ist bekannt?

(schriftliche Publikation, Darstellung, öffentlicher Gebrauch, Produkt usw... bitte belegen!)

8.8.1957 2,566,223 ^{alt} geringerer Druck, Schleppmittel

Datum:

Unterschrift:

Hr. Dr. Frank Schröder

Fr. Bogner, ☎ 2511

Ihre Erfindungsmeldung vom _____ (Eingang PTK/Patente)

Wir bestätigen den Erhalt Ihrer Erfindungsmeldung betreffend

"Melaminsynthese im Rohrreaktor".

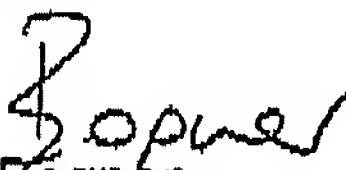
Die Erfindung wird von der Firma Agrolinz Melamin GmbH unbeschränkt in Anspruch genommen. Damit gehen alle Rechte an der Erfindung an diese Firma über.
Die Erfindung wird AMG-intern unter

O.Z. 1230 Kurzwort: "Melamin Rohrreaktor"

bearbeitet.

In der Beilage senden wir Ihnen den Erfinderfragebogen, den wir Sie bitten, auszufüllen und mit den Originalunterschriften aller Erfinder zu retournieren. Wir bitten Sie, den Erhalt dieses Schreibens durch Unterzeichnung und Rücksendung des beiliegenden Doppels an PTK/Patente zu bestätigen.

I.A.


Bogner

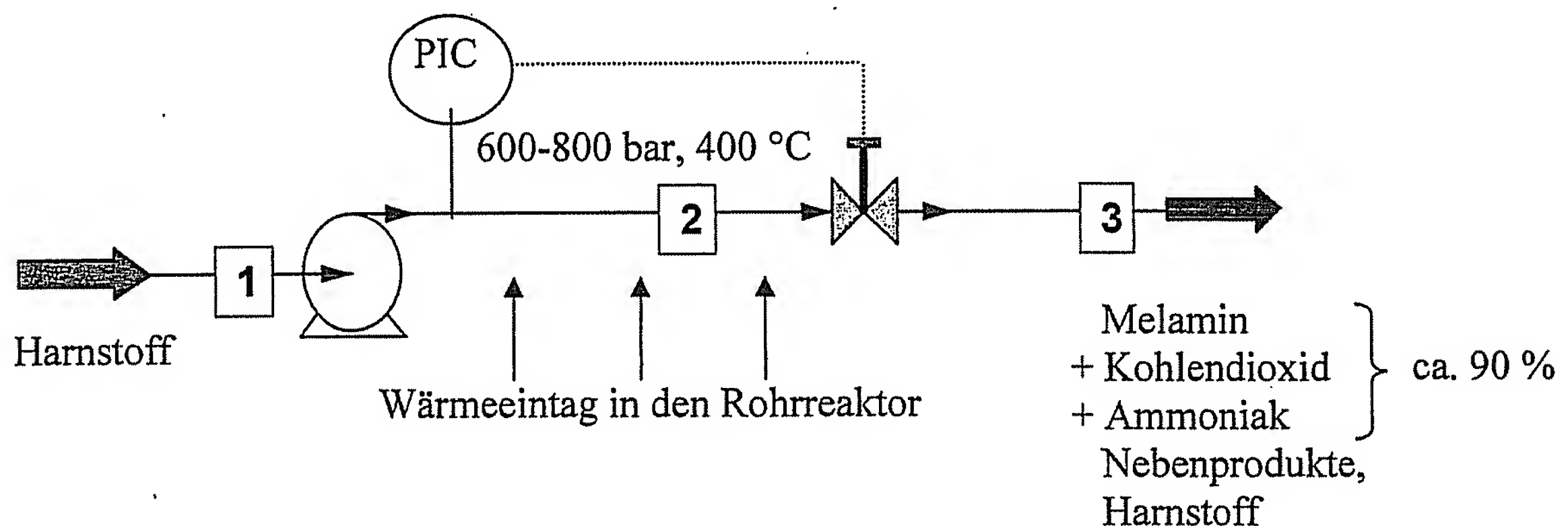
Anlage

..... 
Datum, Unterschrift

Melaminsynthese in einer kontinuierlichen Phase im Rohrreaktor aus Harnstoff

Problem: Beim herkömmlichen Melaminprozess ist die Durchführung im Rohrreaktor wegen der starken Offgasbildung nicht möglich, das Offgas schiebt den nicht umgesetzten Harnstoff zu schnell aus dem Rohr, für die Phasenseparation und den Wärmeübergang bei relativ geringer Fließgeschwindigkeit wird sehr viel Volumen gebraucht.

Lösung: Durch sehr hohen Druck lässt sich aus Melamin Harnstoff und Offgas eine homogene Phase erzeugen. Diese kann bei hoher Turbulenz als Pfropfen durch einen Rohrreaktor gepresst werden. So wird ein sehr intensiver Wärmeübergang erreicht.



Vorteile:

- Geringer Anlagenaufwand im Hochdruckteil (nur Pumpe, beheiztes Rohr, Ventil)
- Geringeres Gefahrenpotential wegen der extrem geringen Reaktorvolumens bei hohem Druck
- Nach bisherigen Messungen geringerer Energieeintrag im Hochdruckteil

Nachteile:

- Nach bisherigen Messungen wahrscheinlich etwas geringerer Umsatz
- Aufarbeitung und Offgasrückführung müssen im Rahmen der Nassteiloptimierung effektiv gelöst werden (wahrscheinlich anders als beim jetzigen Verfahren).

Neuheit:

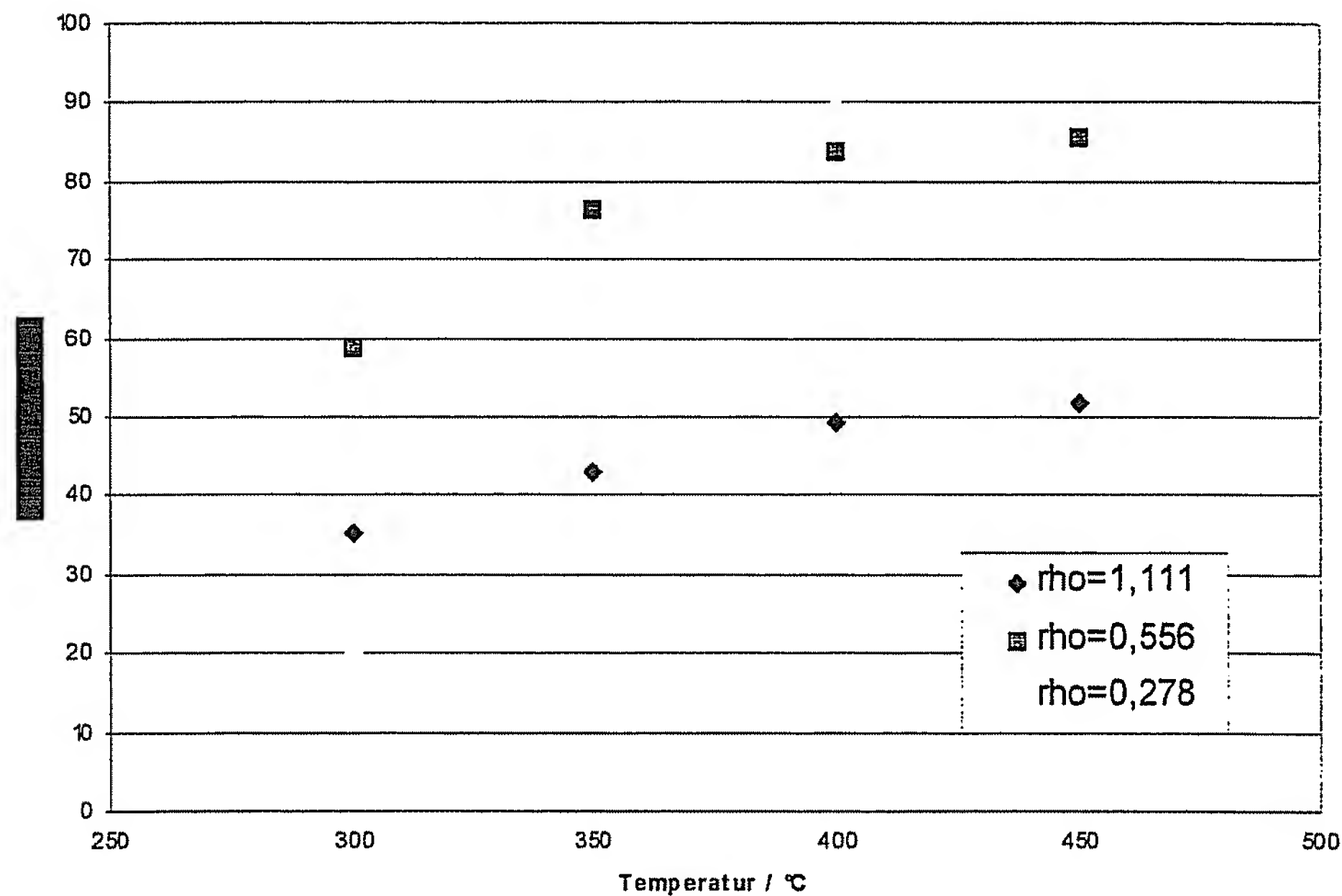
- Einphasige Prozessführung unter so hohem Druck im Rohrreaktor

Stand der Technik:

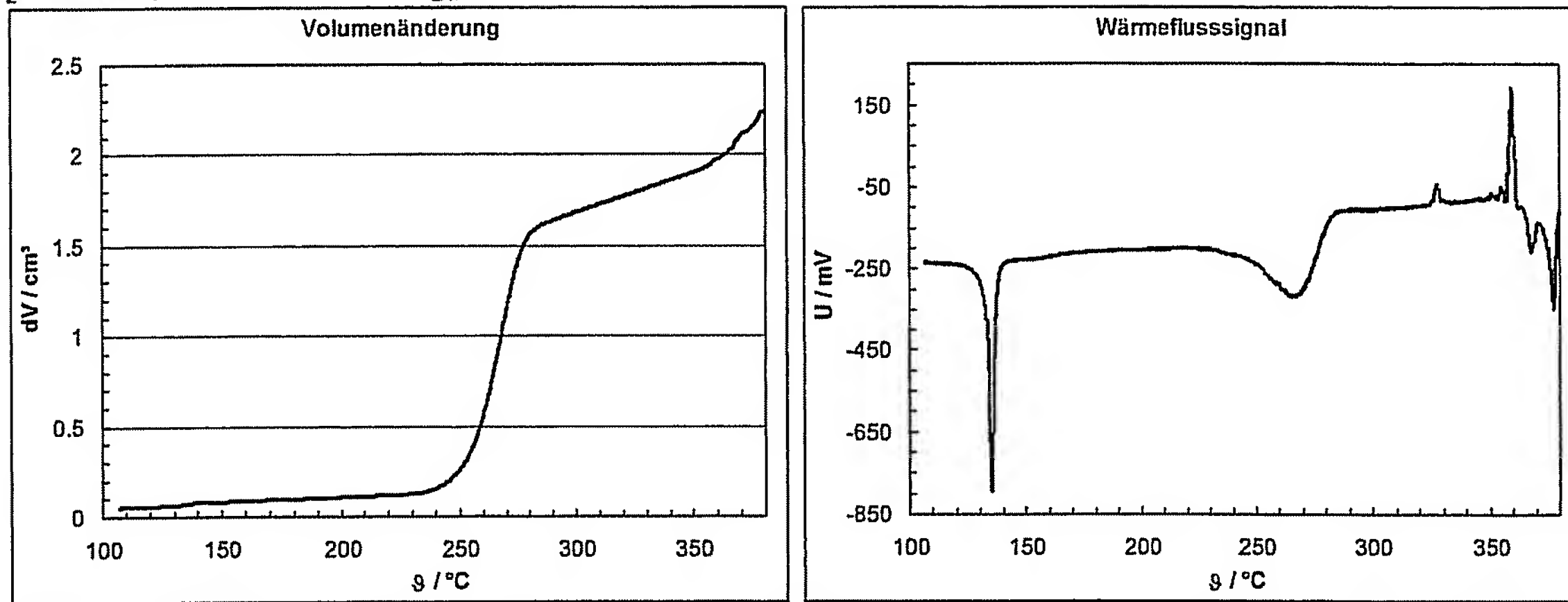
- 28.08.1951 2,566,223 jedoch wesentlich geringerer Druck und Schleppmittel, teilweise höhere Temperatur

Voruntersuchungen

- Prinzipielle Vorversuche gekoppelt mit Materialuntersuchungen (Zusammensetzung wird als Funktion der Temperatur und der Dichte bestimmt) Ergebnis: Bei Inkaufnahme einer gewissen Umsatzreduktion scheint der Prozess einphasig führbar zu sein, was Voraussetzung für die Anwendung eines relativ kleinen Rohrreaktors bei etwa 400 °C ist, Titan-Werkstoffe kommen in Betracht.



Der Umsatz nimmt mit der Temperatur zu und mit der Dichte (dem Druck) ab.



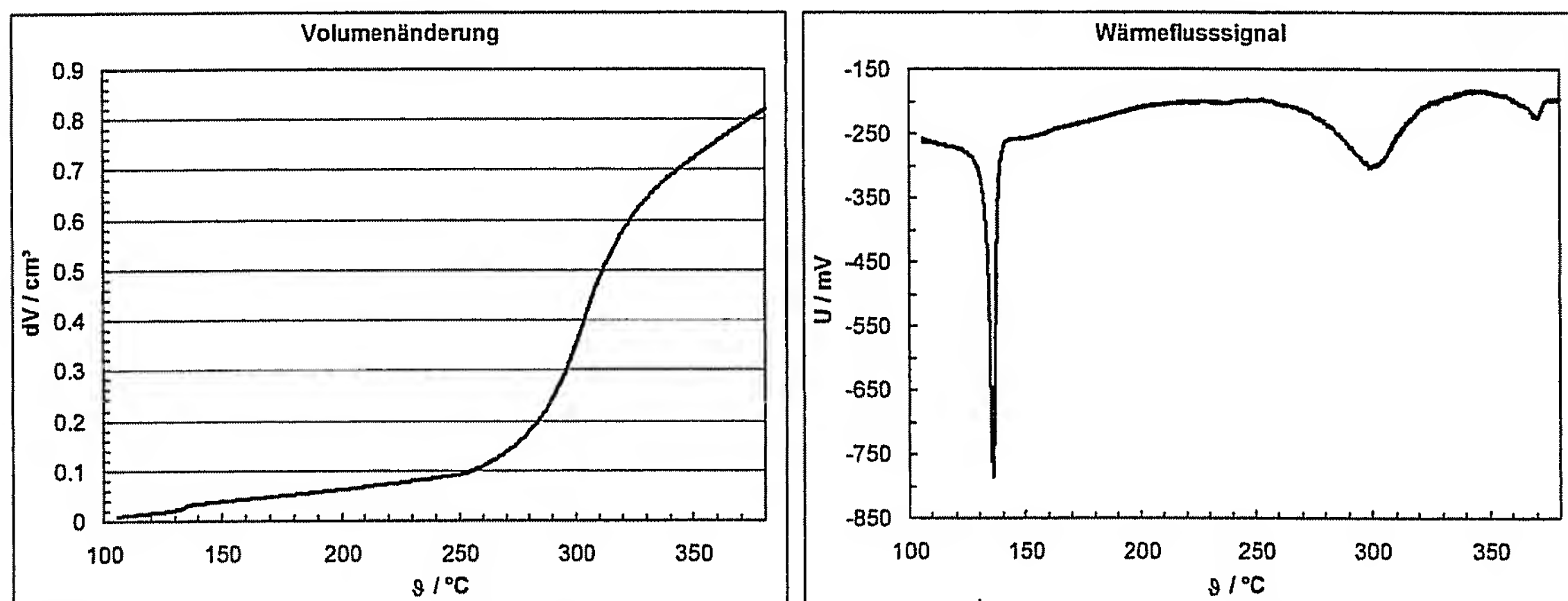
Volumenänderung und Wärme-flusssignal während der Messung bei 130 bar

Heftige Verdampfung bei ca. 265 °C,

Expansion über 350°C

wahrscheinlich Zerfall Harnstoff in Ammoniak
und Isocyan-säure endotherm

Wahrscheinlich Kohlendioxidabspaltung bei
Melaminbildung exotherm, weitere endotherme
Peaks unklar



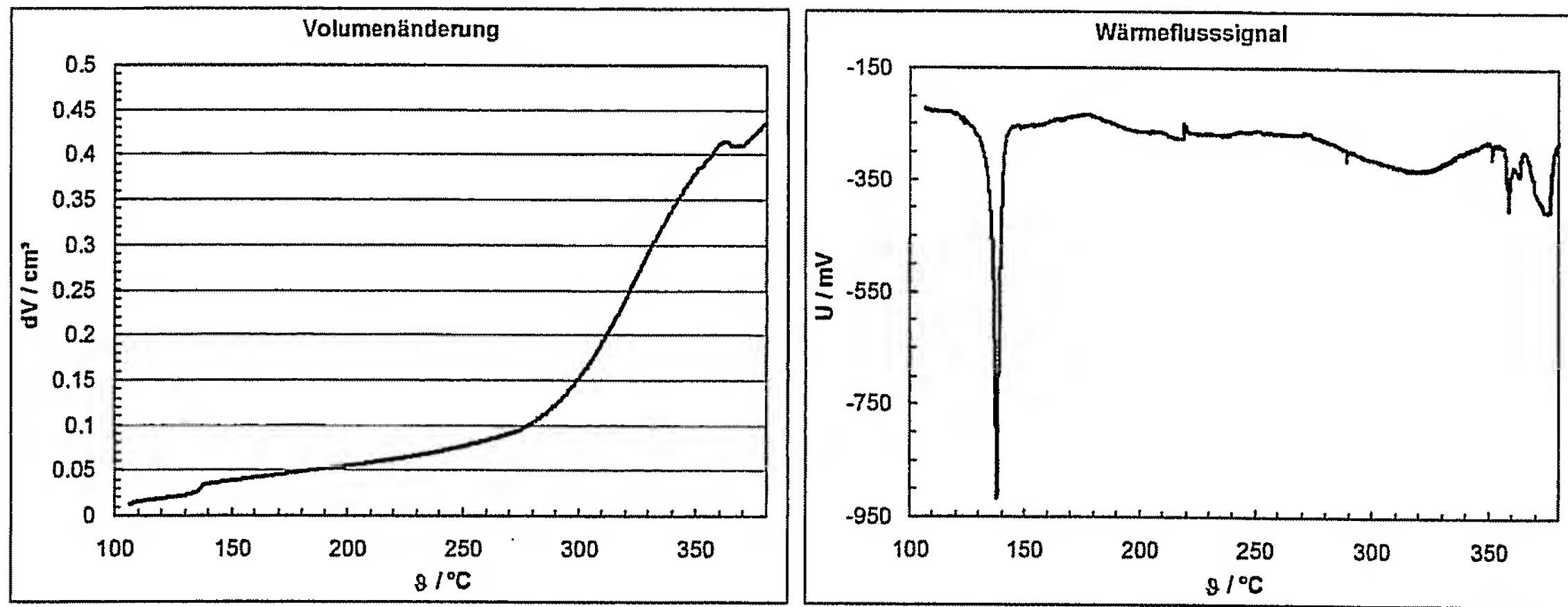
Volumenänderung und Wärme-flusssignal während der Messung bei 350 bar

Heftige Verdampfung bei ca. 300 °C,

Expansion über 350°C

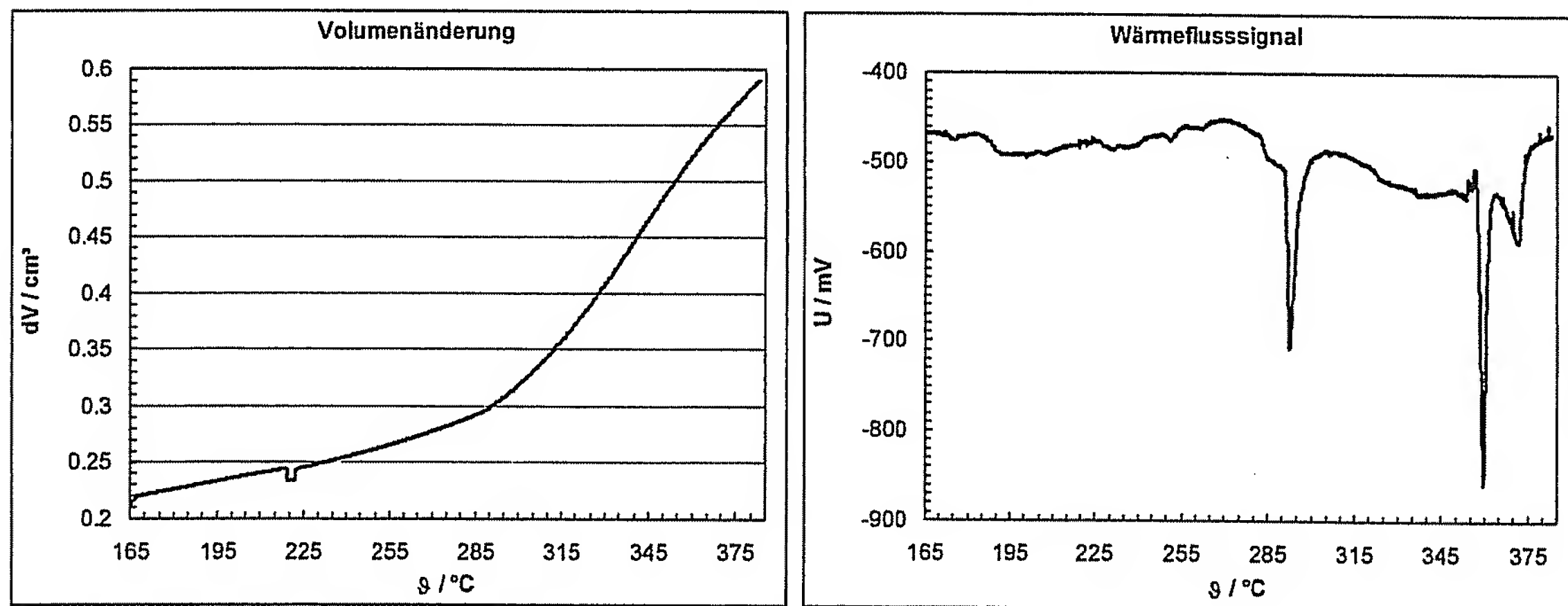
wahrscheinlich Zerfall Harnstoff in Ammoniak
und Isocyan-säure endotherm

Wahrscheinlich Kohlendioxidabspaltung bei
Melaminbildung, Peaks unklar



Volumenänderung und Wärmeflusssignal während der Messung bei 600 bar

Verdampfung bei 300 bis 350 °C undeutlich, wahrscheinlich Zerfall Harnstoff in Ammoniak und Isocyansäure endotherm



Volumenänderung und Wärmeflusssignal während der Messung bei 800 bar

Langsame geringe Expansion,
kein Phasenübergang

mehrere endotherme Reaktionen

Tabelle 1:

P / bar	T _{max,Reaktion}	ΔH / [J/g (Harnstoff)]
130	265.4	588.5
350	300	460
600	318.7	292
800	291.5	99.5

Die genaue Bestimmung der Reaktionsenthalpie ist schwierig, die Werte sind sicher ungenau und den entsprechenden Teilreaktionen nicht eindeutig zugeordnet. Die Tendenz, dass die Reaktionsenthalpie mit steigendem Druck abnimmt weil es keine Verdampfung (Phasenübergang) mehr gibt, ist, wie theoretisch vorhergesagt, erkennbar.

Damit sind die wesentlichen Ziele für das Jahr 2002 erreicht.

Wie kann die Reaktionsenthalpie sinken, die Natur schenkt nichts?

Wenn vorausgesetzt wird, dass die Wärme zur Aufheizung der Ausgangsstoffe bis zur Reaktionstemperatur und die bei der Kühlung der Produkte bis zur Vergleichstemperatur gleichen Betrag haben, kann die Reaktionsenthalpie näherungsweise aus den Bildungsenthalpien berechnet werden:

Synthese bei 130 bar:



$$Q = 6 \cdot 333,99 \text{ kJ/mol} - 71,72 \text{ kJ/mol} - 3 \cdot 393,79 \text{ kJ/mol} - 6 \cdot 42,69 \text{ kJ/mol} = +494,71 \text{ kJ/mol}$$

Ein beträchtlicher Teil dieser Wärme wird durch Volumenarbeit verbraucht, es werden 9 mol Gas pro mol Melamin gebildet.

Synthese bei hohem Druck (600 – 800 bar):

Durch hohen Druck wird wahrscheinlich zum großen Teil Ammoncarbamat gebildet



$$Q = 6 \cdot 333,99 \text{ kJ/mol} - 71,72 \text{ kJ/mol} - 3 \cdot 645 \text{ kJ/mol} = -2,78 \text{ kJ/mol}$$

Es ist zu erwarten, dass wegen der geringeren gemessenen Reaktionenthalpie ein erheblicher Teil des Offgases in Form von Carbamat (weißes Pulver ähnlich wie Melamin) anfällt. So wären die gemessenen geringeren Reaktionsenthalpie theoretisch erklärbar.

RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, hereby declares that, to the best of its knowledge and belief, the following document, prepared by one of its translators competent in the art and conversant with the English and German languages, is a true and correct translation of the accompanying document in the German language.

Signed this 24th day of October 2007

C. E. SITCH


Managing Director - UK Translation Division

For and on behalf of RWS Group Ltd

EXHIBIT B

Notice of invention		1230
		Melamine tubular reactor
		--
To be filled out by the (main) inventor:		
I hereby announce the invention described below, for which I request application for patent protection in the name of Agrolinz Melamin GmbH.		
CONFIDENTIAL		
10. Subject matter of the invention:		
Title of the draft of the patent application:	Melamine synthesis in a continuous phase in a tubular reactor from urea	
11. Technical problem addressed by the invention?		
Obtaining melamine in a continuous phase in a tubular reactor - lower heat of reaction - lower expenditure in the HP part - lower risk potential as a result of short residence time in the HP part		
12. Description of the invention:		
Urea	Pump 600-800 bar, approx. 400°C	Tubular reactor Melamine $\text{CO}_2 \text{ NH}_3 \text{ NH}_2\text{COONH}_4$ Urea (up to 15%)
13. What is the novelty and the advantage of the invention?		
Novelty:	Monophasic process under such high pressure in the tubular reactor	
Advantage(s):	Lower heat of reaction, lower expenditure in the HP part, lower risk potential as a result of short residence time in the HP part	
14. What prior art is known?		
(please enclose written publication, presentation, public use, product, etc!)		
28.8.1951	2,566,223	but lower pressure, azeotroping agent
Date:	Signature: [signature]	

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RECEIVED BY PT

Dr. Frank Schröder

PTK/Bo

Ms. Bogner, ☎ 2511

Your notice of invention of _____ (received by PTK/Patents)

We confirm that we have received your notice of invention relating to

"Melamine synthesis in a tubular reactor".

The invention will be taken on without restriction by Agrolinz Melamin GmbH. All rights to the invention are thus transferred to this company. The invention will be processed within AMG under

O.Z. 1230 short name: "Melamine tubular reactor".

We enclose the inventor's questionnaire, which we request you to fill in and return with the original signatures of all inventors. We ask you to confirm that you have received this letter by signing and returning the enclosed copy to PTK/Patents.

pp.

[signature]

Bogner

Enclosure

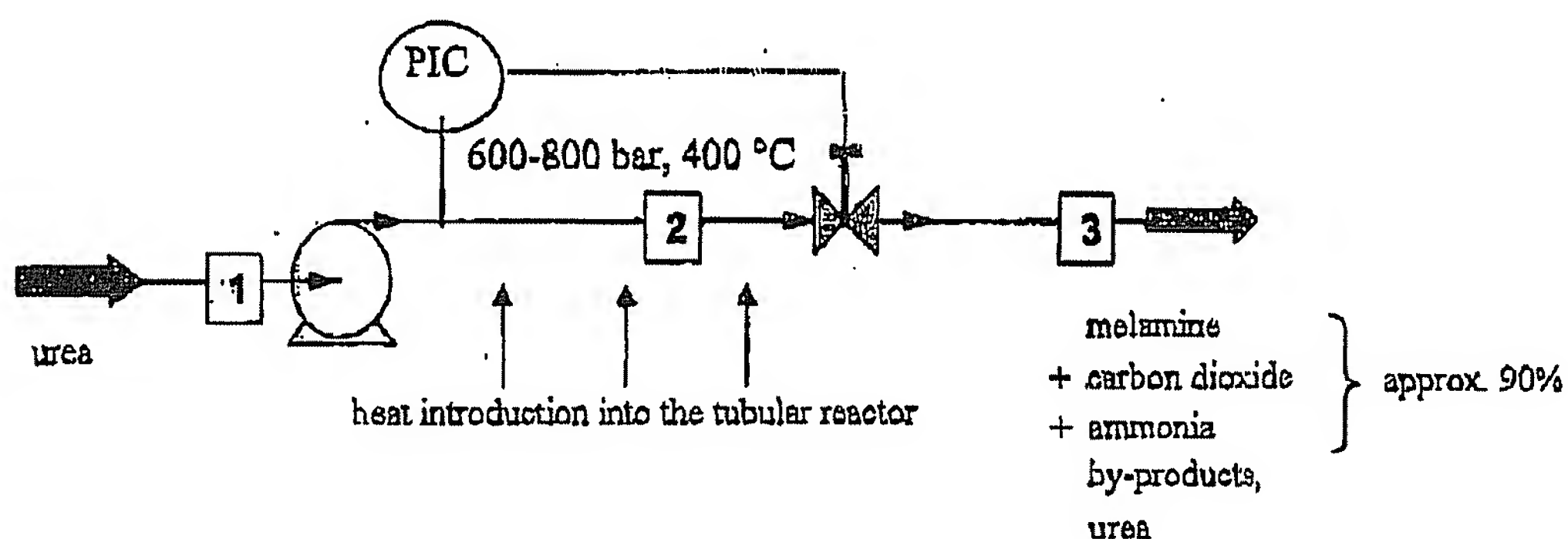
[signature]

Date, signature

Melamine synthesis in a continuous phase in a tubular reactor from urea

Problem: In the conventional melamine process, performance in a tubular reactor is not possible owing to the high offgas formation; the offgas shifts the unconverted urea out of the tube too rapidly; for the phase separation and the heat transfer at relatively low flow rate, a very large volume is needed.

Solution: As a result of very high pressure, it is possible to obtain a homogeneous phase from melamine, urea and offgas. This can be compressed at high turbulence as a plug through a tubular reactor. Very intensive heat transfer is thus achieved.



Advantages:

- Low plant complexity in the high-pressure part (only pump, heated tube, valve)
- Lower risk potential owing to the extremely low reactor volume at high pressure
- According to measurements to date, lower energy input in the high-pressure part

Disadvantages:

- According to measurements to date, probably somewhat lower conversion
- Workup and offgas recycling have to be solved effectively in the context of the wet-part optimization (probably in a different way to that in the current process).

Novelty:

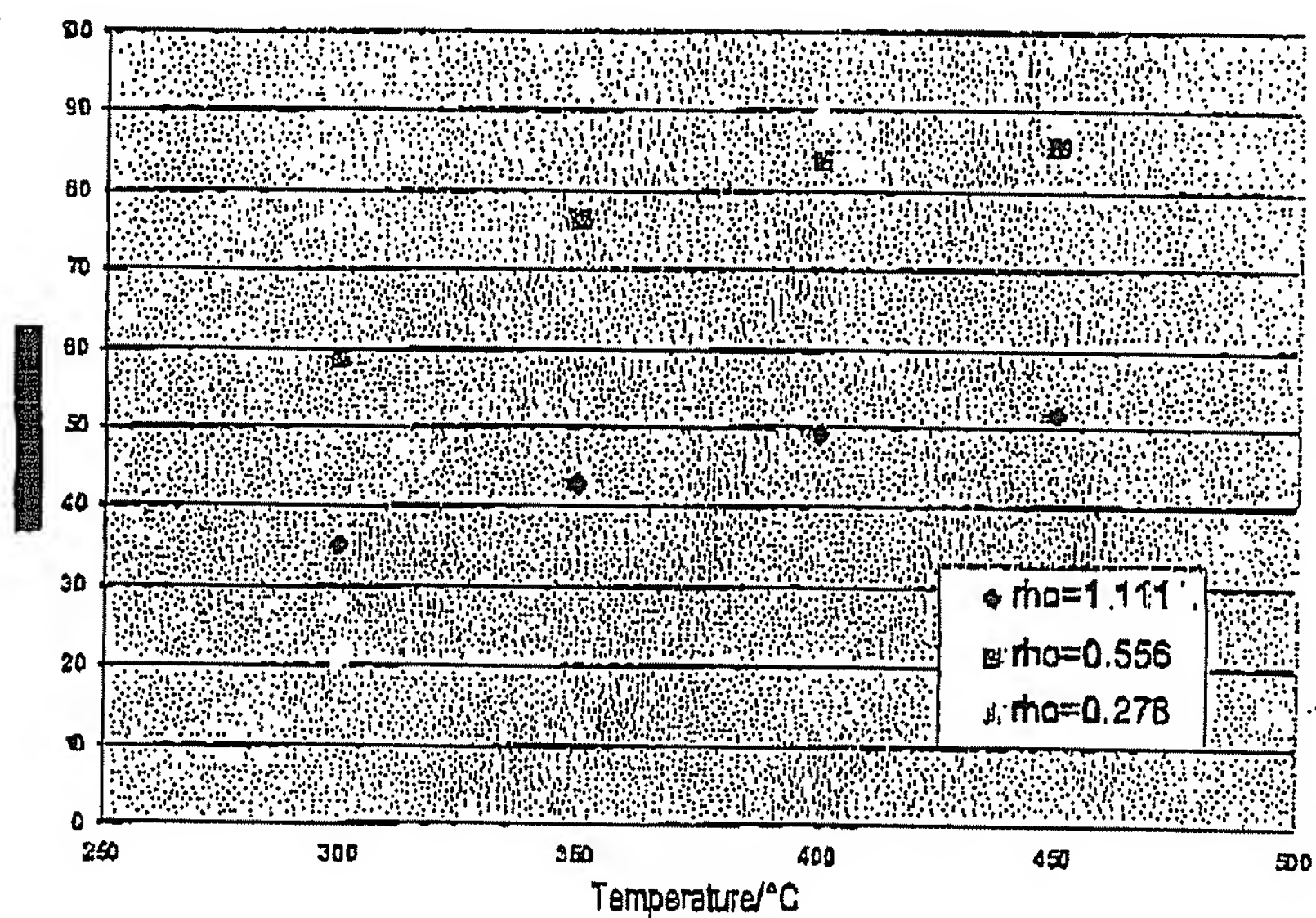
- Monophasic process under such high pressure in the tubular reactor

Prior art:

- 28.08.1951 2,566,223, but significantly lower pressure and azeotroping agent, in some cases higher temperature

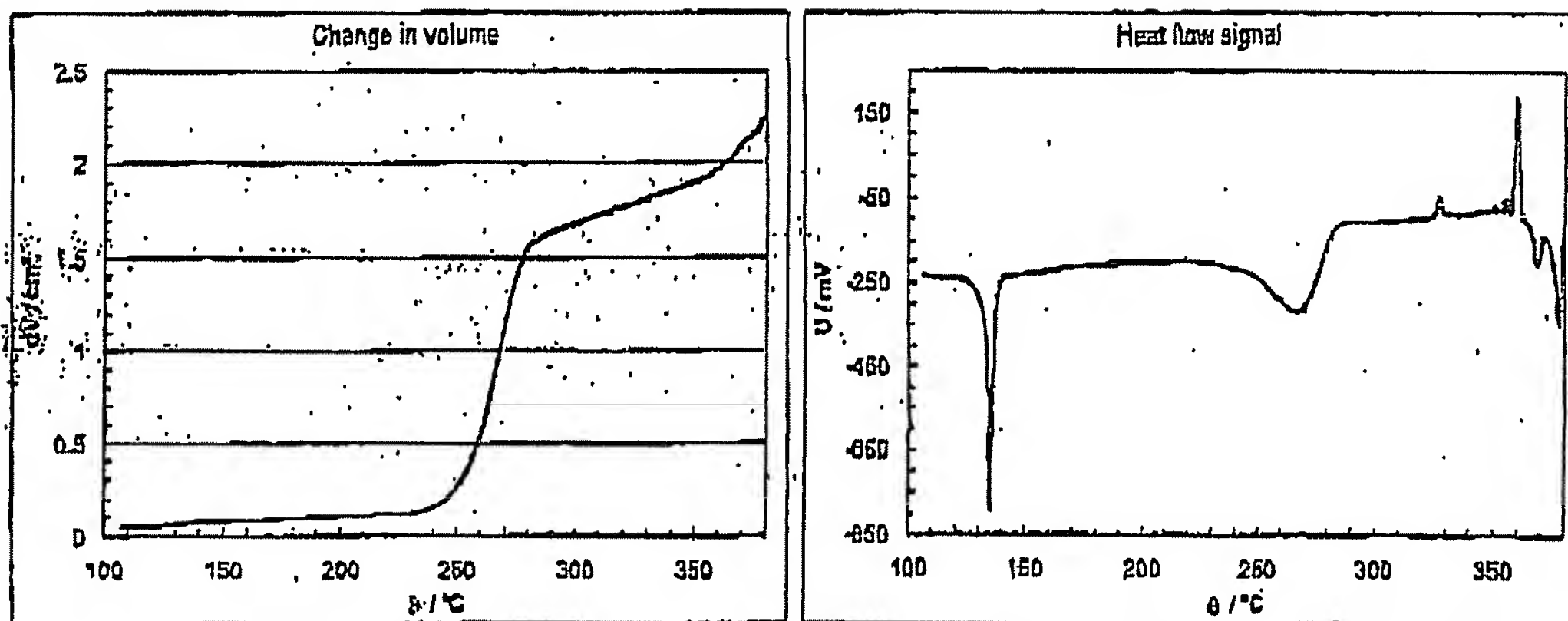
Preliminary Investigations

- Preliminary tests in principle coupled with material examinations (composition is determined as a function of the temperature and of the density). Result: If a certain reduction in conversion is accepted, the process appears to be conductible in a monophasic method, which is a prerequisite for the application of a relatively small tubular reactor at about 400°C; titanium materials are possible.



The conversion increases with temperature and decreases with density (the pressure).

[Fischer, Oldenburg University]



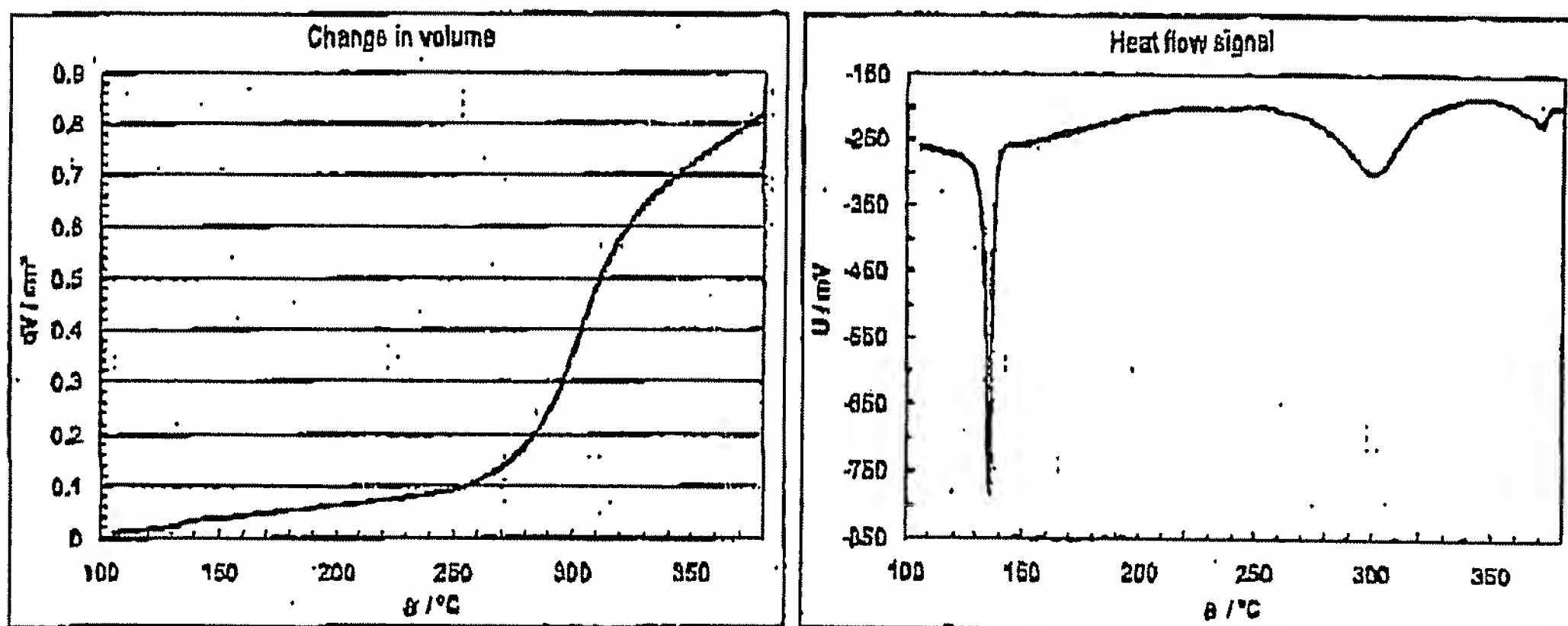
Change in volume and heat flow signal during measurement at 130 bar

Vigorous evaporation at approx. 265°C

probably decomposition of urea to ammonia and isocyanuric acid, endothermic

Expansion above 350°C

probably carbon dioxide elimination with melamine formation, exothermic, further endothermic peaks unclear



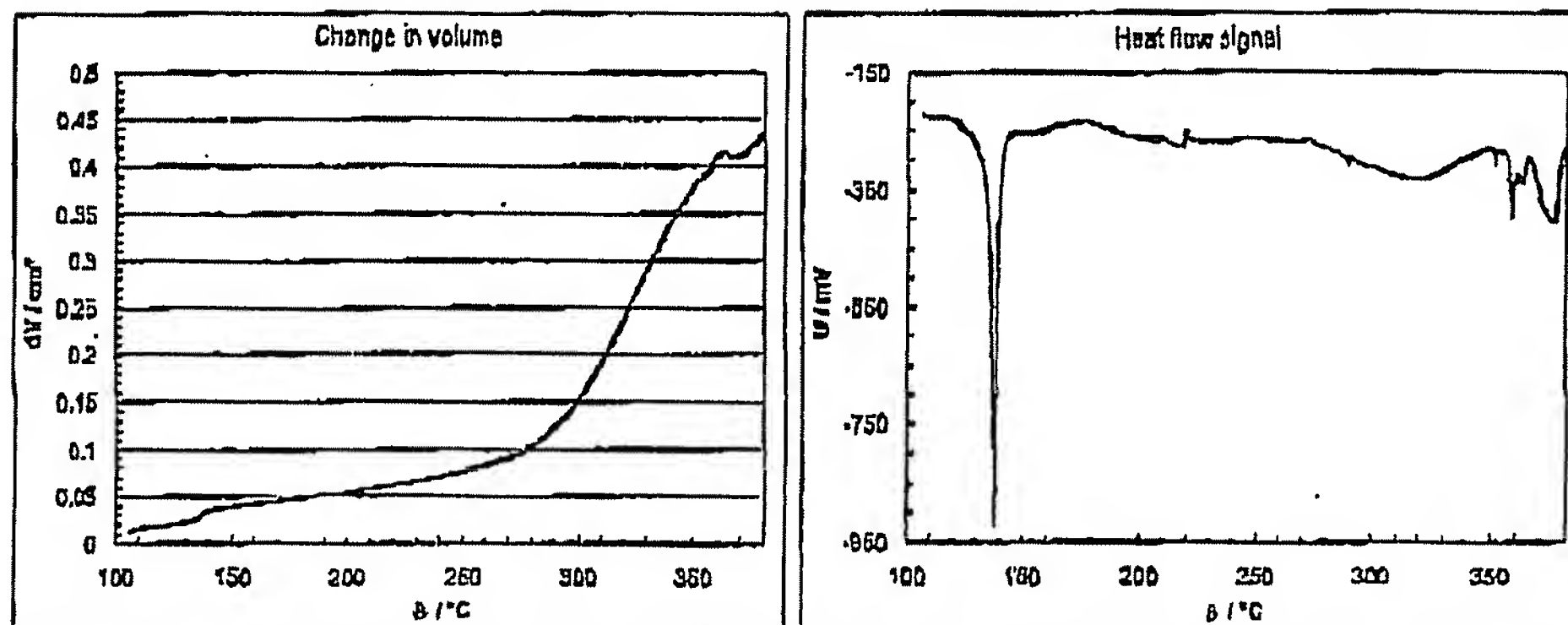
Change in volume and heat flow signal during measurement at 350 bar

Vigorous evaporation at approx. 300°C

probably decomposition of urea to ammonia and isocyanuric acid, endothermic

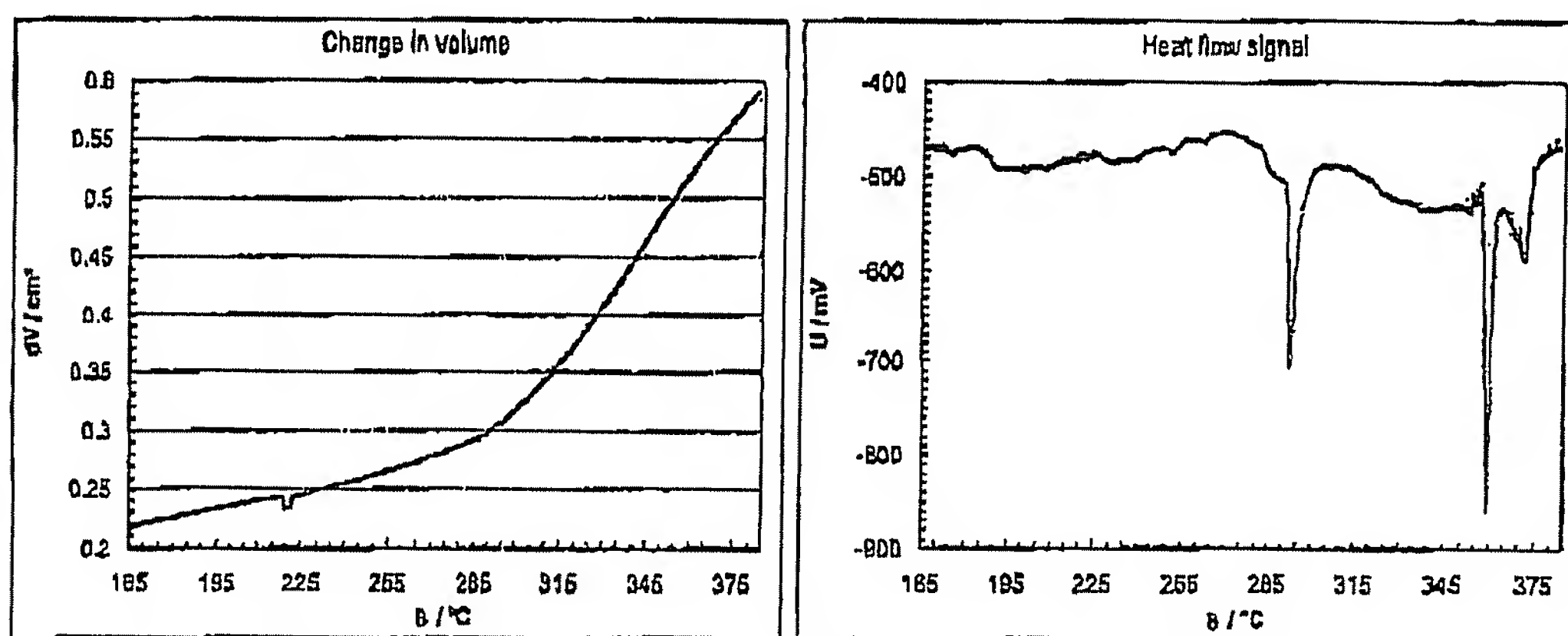
Expansion above 350°C

probably carbon dioxide elimination with melamine formation, peaks unclear



Change in volume and heat flow signal during measurement at 600 bar

Evaporation at from 300 to 350°C unclear, probably decomposition of urea to ammonia and isocyanuric acid, endothermic



Change in volume and heat flow signal during measurement at 800 bar

Slow gentle expansion, no phase transition several endothermic reactions

Table I:

P/bar	$T_{\text{max, reaction}}$	ΔH [J/g (urea)]
130	265.4	588.5
350	300	460
600	318.7	292
800	291.5	99.5

The exact determination of the reaction enthalpy is difficult; the values are certainly inexact and the corresponding part-reactions cannot be assigned unambiguously. The trend that the reaction enthalpy decreases with rising pressure because there is no longer any evaporation (phase transition) is, as forecast theoretically, discernible.

The significant aims for 2002 have thus been achieved.

How can the reaction enthalpy fall? Nature does not give any presents.

If it is assumed that the heat for heating the starting materials up to the reaction temperature and that in the cooling of the products down to the comparative temperature have the same magnitude, the reaction enthalpy can be calculated approximately from the enthalpies of formation:

Synthesis at 130 bar:



$$Q = 6 \cdot 333.99 \text{ kJ/mol} - 71.72 \text{ kJ/mol} - 3 \cdot 393.79 \text{ kJ/mol} - 6 \cdot 42.69 \text{ kJ/mol} = +494.71 \text{ kJ/mol}$$

A considerable part of this heat is consumed by volume work; 9 mol of gas are formed per mol of melamine.

Synthesis at high pressure (600 - 800 bar):

As a result of high pressure, ammonium carbamate is probably formed to a high degree



$$Q = 6 \cdot 333.99 \text{ kJ/mol} - 71.72 \text{ kJ/mol} - 3 \cdot 645 \text{ kJ/mol} = -2.78 \text{ kJ/mol}$$

It is expected that, owing to the lower reaction enthalpy measured, a considerable part of the offgas is obtained in the form of carbamate (white powder similar to melamine). The lower reaction enthalpies measured would thus be explicable theoretically.